CHAPTER II

THEORY

2.1 Gasohol

Gasohol is one of the most interesting alternative fuels because it is cheaper than gasoline and environmentally friendly due to its perfect combustion. Gasohol is a blend of gasoline and pure alcohol at different ratio. Ethanol fuel mixtures have "E" numbers which describe the percentage by volume of ethanol in the mixture, for example, E85 has 85 vol% ethanol and 15 vol% gasoline. The proportion of ethanol used in gasohol is generally 10 vol%.

Gasohol (E10) has the same characteristics as octane 95 unleaded gasoline (benzene 95), except that the oxygenated compound, normally, MTBE (Methyl Tertiary Butyl Ether) that is required by regulation to be added to octane 95 unleaded gasoline at a 5.511 vol%, is replaced by 99.5% pure alcohol at the 10-11 vol%. In gasohol, ethanol serves as an additive to enhance oxygenate value and octane number of gasoline [13]. Therefore, gasohol has higher octane or antiknock properties than gasoline and burns more slowly, coolly, and completely. Oxygen in ethanol causes the combustion of gasohol to produce lower levels of hydrocarbons, carbon monoxide and carbon dioxide than general octane 95 gasoline, and helps to reduce black smoke, aromatic hydrocarbons, benzene, and dust emission from exhaust pipes [14].

E10 is used globally, including Thailand, because this proportion of mixture can be used in vehicles without engines modification. However, many countries are now trying to promote the use of ethanol by mixing it at a higher proportion with gasoline. Brazil is one such country, which embraces ethanol blend from 20 percent (E20) up to pure ethanol (E100). Besides, the United States, Canada and Sweden also use Gasohol 85, which has only 15 vol% of gasoline in its mixture. The gasoline content is kept in this formula because it helps engines to start easily during the cold weather. Gasohol with

85 percent concentration of ethanol has an octane rating as high as 105, which can boost the performances of the vehicle engine [13].

2.1.1 Alcohol in Gasohol

Alcohol is an alternative transportation fuel since it has properties that would allow its use in existing engines with minor hardware modifications. Alcohol has an octane number higher than that of gasoline. A fuel with a higher octane number can endure higher compression ratio before engine starts knocking. Engine compression ratio is the relative volume of a cylinder from the bottom most position of the piston's stroke to the top most position of the piston's stroke. The higher an engine's compression ratio, the greater the amount of heat generated in the cylinder during the compression stroke, thus a fuel with a higher octane number gives engine an ability to deliver more power efficiently and economically. Alcohols burns cleaner than regular gasoline and produce lesser carbon monoxide, hydrocarbons and oxides of nitrogen [15-17].

Methanol (CH_3OH) and ethanol (C_2H_5OH) are simple compounds that possess less flammability and give higher engine efficiency than gasoline. However, ethanol is considerably cleaner, less toxic, less corrosive and gives greater engine efficiency than methanol. Ethanol is a grain alcohol and can be produced from fermentation of sugar cane, cassava and other grains, to convert starch into sugar and then alcohol, respectively. The purification of alcohol by distillation is used to attain a pure alcohol of 95 vol%. Ethanol for blending with fuel to fill in the car engine is a pure alcohol of 99.5 vol% which is capable of using as fuel [2,3].

The primary disadvantage of mixing methyl or ethyl alcohol with gasoline is that under certain conditions these alcohols may phase separate from the gasoline. Hence, an engine adjusted to burn gasoline efficiently will produce less power from alcohol/gasoline mixture. Phase separation is caused by the different in polar nature of the alcohol molecules and their tendency to absorb water, also a polar substance. Methyl alcohol is the most likely to separate, while butyl alcohol is the least likely. The tendency for phase separation increases as the temperature decreases, the quantity of water absorbed increases, and the quality of the gasoline decreases [10].

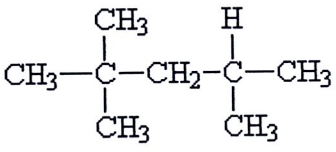
2.1.2 Gasoline

Gasoline is a petroleum-derived liquid mixture that is primarily used as fuel in internal combustion engines. It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum. Small quantities of various additives are common for specific purposes such as tuning engine performance or reducing harmful exhaust emissions. Some mixtures also contain significant quantities of ethanol as partial alternative fuel.

Octane rating

An important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as pre-detonation (also known as knocking, pinging, spark knock, and other names). Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptane. Octane rating of gasoline can be improved by incorporating isooctane or aromatic hydrocarbons such as toluene and benzene.

2,2,4-trimethylpentane (Isooctane)



$$\begin{array}{ccccccc} & & CH_3 & & H & & \\ & & | & & | & & \\ CH_3 & - & C & -CH_2- & C & - & CH_3 \\ & & | & & | & & \\ & & CH_3 & & CH_3 & & \end{array}$$

Figure 2.1 Structure of isooctane (2,2,4-trimethylpentane)

Isooctane or 2,2,4-trimethylpentane is octane isomer which defines as the 100 point on the octane rating scale compared with that of n-heptane. It is a highly branched compound that burns smoothly, with little knocking. This isooctane is particularly useful in the formulation of gasoline containing ethanol in direct blending, for example in those produced in the United States, owing to its extremely low volatility that counterbalances the very high volatility of ethanol [11].

Toluene

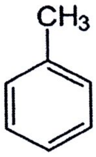


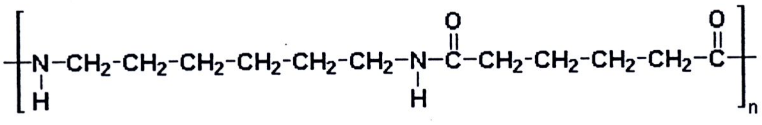
Figure 2.2 Structure of toluene (methylbenzene) [18]

Toluene (methylbenzene) is a clear water-insoluble liquid with the typical smell of paint thinners. It is an aromatic hydrocarbon (C_7H_8) that occurs naturally at low levels in crude oil and is usually produced in the process of making gasoline via a catalytic reformer, and in an ethylene cracker or making coke from coal. Final separation (either via distillation or solvent extraction) takes place in a Benzene Toluene Xylene (BTX) plant [18,19].

Toluene can be used as an octane booster in gasoline fuels in internal combustion engines. Toluene at 100% can be used as a fuel for both two-stroke and four-stroke engines; however, due to the density of the fuel and other factors, the fuel does not vaporize easily unless preheated to 70 degree Celsius. Toluene also poses similar problems as alcohol fuels, as it flows through standard rubber fuel lines and has no lubricating properties as standard gasoline which can break down fuel pumps and causes upper cylinder bore wear [18].

2.2 Polyamide 6 or Nylon 6 (PA6)

Polyamide is the chemical name for nylon. Nylon is made of repeating units with amide linkages. Nylon is classified into the largest family of engineering plastics with a very wide range of applications. It is derived from the reaction of diamine and dicarboxylic acid. Because of a variety of chemical structures of diamine and dicarboxylic acid, there are a very large number of nylon materials available to produce nylon fibers. There are several commercial nylon products, such as nylon 6, nylon 11, nylon 12, nylon 6,6, nylon 6,10 and so on. The numbers usually appended to the "nylon" or "PA" part refer to the number of CH units between the reactive ends of the monomer [12]. Nylon 6,6 refers to the fact that both the diamine (hexamethylene diamine) and the diacid (adipic acid) have 6 carbon backbones [9,12], as shown in Figure 2.3. The two most important kinds of nylon are nylon 6 and nylon 6,6 and account for more than 90% of nylon use. Characteristic nylons are very resistant to wear and abrasion, have good mechanical properties even at elevated temperatures, have low permeability to gases and have good chemical resistance, but will absorb moisture, particularly nylon 6 and nylon 6,6. Because nylons offer good mechanical and thermal properties, they are also a very important engineering thermoplastic. For example, 35% of total nylon produced is used in the automobile industry [20-23].



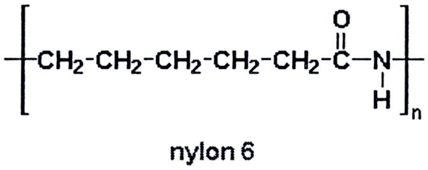
$$\left[-\underset{\mathrm{H}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]_n$$

nylon 6-6

Figure 2.3 Repeating unit of nylon 6,6 [20]

Nylon 6 (PA6) and nylon 6,6 (PA6,6) were invented in the late 1930s. Nylon 6,6 was discovered first. It was invented in the United States by Wallace Carothers who was working for DuPont. Not long after that nylon 6 was invented in Germany by Paul Schlack who was working for I.G. Farben. Nylon 6, unlike most other nylons which were made from dicarboxylic acid and diamine, is made from one kind of monomer, such as a cyclic amide, by ring-opening polymerization. This makes it a special case in the composition between condensation and addition polymers. Its competition with nylon 6,6 and the example it set have also shaped the economics of the synthetic fiber industry [24,25].

Nylon 6, with structure shown in Figure 2.4, is well-known as providing the best price/performance ratio of engineering plastics. This explains why nylon 6 is extensively used in automotive to optimize system cost [26]. Nylon 6 is easier to process by injection molding than nylon 6,6. It has lower mold shrinkage than nylon 6,6 with good fatigue resistance. Useful improvement in stiffness can be obtained by inclusion of glass fiber [12,27]. Nylon 6 is as stiff as nylon 6,6 with temperatures up to 180 °C and also exhibits a better long-term heat aging than nylon 6,6. Additionally, nylon 6 is cheaper than nylon 6,6 in terms of basic cost and provides a better surface appearance and a better weld strength which leads to a better burst pressure resistance. From these reasons, nylon 6 is a better candidate than nylon 6,6 [28].



$$-\!\!\left[CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}\right]_n\!\!-$$

Figure 2.4 Repeating unit of nylon 6 [20]

2.2.1 Production of Nylon 6

Generally, nylons are made from a condensation polymerization using two different monomers, e.g. dicarboxylic acid and diamine. But nylon 6 is made from only one kind of monomer, such as a cyclic amide called lactum. Caprolactum is a lactum with six carbon atoms, so nylon made from caprolactum is called nylon 6 or polyamide 6 (PA6) [20]. PA6 can be produced by chain-growth polymerization of lactams which is one kind of the ring-opening polymerization. It is also a polyaddition reaction with no byproduct formed. There are two ways to carry out a ring-opening polymerization of caprolactum. The first way to make PA6 is to use a water-initiated process and the second way is to use a strong base as initiator. A strong base as initiator will not work well without poly(ethylene oxide) or N-acetylcaprolactum. By adding the strong base, high molecular weight PA6 after heating the mixture for 2-3 minutes can be obtained. Nevertheless, heating the mixture too long causes the thermally degradation resulting in lowering molecular weight of desired PA6 [25].

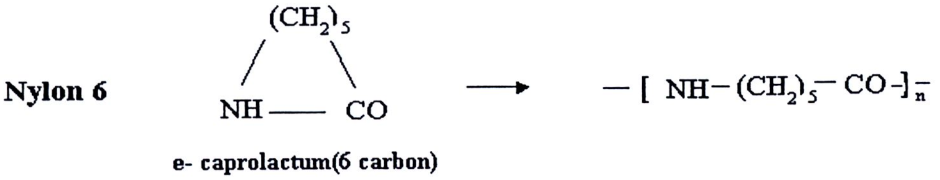


Figure 2.5 Chemical reaction for produce PA6 [20]

During polymerization, the peptide bond within each caprolactum molecule is broken reforming two new bonds as the monomer becomes part of the polymer backbone. PA6 therefore resembles natural polypeptides more closely; in fact, caprolactum would become an amino acid if it were hydrolyzed [24].

2.2.2 Properties of Nylon 6

Nylon is a semi-crystalline polymer. The amide group (-CO-NH-) provides hydrogen bonding between polyamide chains. The nitrogen-bonded hydrogens of one nylon chain will hydrogen bond very strong with the carbonyl oxygens of another nylon chain. These hydrogen bonds make crystals of nylon very strong because they hold the nylon chains together very tightly. These strong crystals make strong fibers [25], giving nylon high strength and toughness at elevated temperatures, and its other properties, such as stiffness, wear and abrasion resistance, low friction coefficient and good chemical resistance [23].

a) Physical properties

Semicrytalline nylon comprises the vast majority of commercial resins. Nylon is also available in an amorphous form that gives rise to transparency and improves toughness at the expense of high temperature and chemical stress-crack resistance.

- Density: Density (ρ) depends on the nature of atoms in the chemical structure and the way molecules (chains) pack together. Conformations and crystalline phases are generally denser than amorphous phases, an average ρ_c / ρ_a ratio of 1.13±0.08 has been determined [9].

- Moisture absorption: A characteristic property of nylon is the ability to absorb significant amount of water. This is related to the polar amide groups which water molecules can become coordinated. Water absorption is generally concentrated in the amorphous regions of the polymer, where it has the effect of plasticizing, by interrupting the polymer hydrogen bonding, making it more flexible (with lower tensile strength) and increasing the impact strength. The T_g is also reduced. PA6 has higher moisture absorption than PA6,6 because of its lower crystallinity.

- Crystallinity: For common nylons such as PA6 and PA6,6, the regular spatial alignment of amide groups allows a high degree of hydrogen bonding to be developed when the chains are able to organize themselves into a crystalline structure [29]. These nylons are semicrystalline materials which consist of ordered crystalline regions and more random amorphous areas having a much lower concentration of hydrogen bonding. This semicrystalline structure gives rise to the good balance of properties. The crystalline regions contribute to the stiffness, strength, chemical resistance, creep resistance, temperature stability, and electrical properties; while the amorphous regions contribute to the impact resistance and high elongation. Table 2.1 showed the physical properties of PA6 and PA6/glass fiber composites at 15% and 30 wt% glass fiber, respectively, as reported by UBE Chemicals (Thailand).

Table 2.1 Physical properties of PA6 and PA6/glass fiber composites [30-32]

Material	Physical properties		State of test	Test method
PA6	Density (g/cm^3)	1.12-1.14	-	ISO 1183
	Specific gravity	1.14	-	ASTM D 792
	Water absorption (%)	8.5-10	Saturated	ASTM D570
		1.3- 1.9	After 24 hrs	ASTM D570
	Mold shrinkage (%)	1.4	MD	UBE method
		1.6	TD	UBE method

Material	Physical properties		State of test	Test method
15 wt% glass fiber reinforced PA6	Specific gravity	1.23	-	ASTM D 792
	Water absorption (%)	8	Saturated	ASTM D570
		1.1-1.6	After 24 hrs	ASTM D570
	Mold shrinkage (%)	0.3	MD	UBE method
		0.7	TD	UBE method
30 wt% glass fiber reinforced PA6	Density (g/cm^3)	1.36	-	ISO 1183
	Specific gravity	1.35-1.42	-	ASTM D 792
	Water absorption (%)	6.4-7	Saturated	ASTM D570
		0.9-1.2	After 24 hrs	ASTM D570
	Mold shrinkage (%)	0.2	MD	UBE method
		0.7	TD	UBE method

Note MD = in flow direction, TD = in perpendicular direction

b) Mechanical and thermal properties

The properties of nylon depend on the type of nylon (including copolymerization), molecular weight, moisture content, temperature, and the presence of additives. In these materials it is the amide group which is responsible for increasing inter chain attraction. Therefore, heat distortion temperature and stiffness can be improved [29]. Strength and modulus (stiffness) are increased by increasing density of amide groups and crystallinity in aliphatic nylons. Increasing molecular weight gives increased impact strength without having a significant effect on tensile strength. Increasing moisture content reduces the T_g, tensile modulus and tensile strength significantly; however, some nylons with a high T_g, such as those containing aromatic monomers, have little change in properties with changing moisture as the T_g remains above room temperature.

Properties such as strength and rigidity can be considerably increased by adding a reinforcing agent to the polymer matrix, particularly glass or carbon fiber. Mechanical properties can also be modified by the inclusion of plasticizers, which have a similar effect to that of water in breaking down hydrogen bonding in the amorphous region and increasing ductility, flexibility, and impact strength. Table 2.2-2.4 showed the mechanical properties of PA6 and PA6/glass fiber composites at 15% and 30 wt% glass fiber, respectively, while Table 2.5 showed the thermal properties of PA6 and PA6/glass fiber composites, as reported by UBE Chemicals (Thailand).

Table 2.2 Mechanical properties of PA6 [30-33]

Mechanical Properties		State of test	Test method
Tensile strength at yield (MPa)	71	Water content 0.2 %	ASTM D638
	49	Water content 3.5 %	ASTM D638
Tensile elongation at break (%)	>200	Water content 0.2 %	ASTM D638
Tensile modulus (MPa)	2300-2500	-	ASTM D638
Flexural strength (MPa)	103	Dry as molded	ASTM D790
Flexural modulus (MPa)	2500	Dry as molded	ASTM D790
Compressive strength (MPa)	46-90	-	ASTM D695
Impact strength (kJ/m^2)	10.98	-	ASTM D256

Table 2.3 Mechanical properties of PA6/15 wt% glass fiber composite [30-33]

Mechanical Properties		**State of test**	**Test method**
Tensile strength at yield (MPa)	125	Water content 0.2 %	ASTM D638
	71	Water content 3.5 %	ASTM D638
Tensile elongation at break (%)	2.8	Water content 0.2 %	ASTM D638
Tensile modulus (MPa)	5800	-	ASTM D638
Flexural strength (MPa)	190	-	ASTM D790
Flexural modulus (MPa)	5300	-	ASTM D790
Impact strength (kJ/m^2)	8.58	-	ASTM D256

Table 2.4 Mechanical properties of PA6/30 wt% glass fiber composite [30-33]

Mechanical Properties		**State of test**	**Test method**
Tensile strength at yield (MPa)	166-190	Water content 0.2 %	ASTM D638
	130	50% relative humidity	ASTM D638
Tensile elongation at break (%)	2-4	Water content 0.2 %	ASTM D638
Tensile modulus (MPa)	7521	-	ASTM D638
Flexural strength (MPa)	235-248	Water content 0.2 %	ASTM D790
	145	50% relative humidity	
Flexural modulus (MPa)	8625-9660	Water content 0.2 %	ASTM D790
Compressive strength (MPa)	131	-	ASTM D695
Impact strength (kJ/m^2)	15	-	ASTM D256

Table 2.5 Thermal properties of PA6 and PA6/glass fiber composites [30-33]

Material	Thermal properties		State of test	Test method
PA6	Melting temperature (°C)	210-225	T_m, crystalline	-
	Glass transition temperature (°C)	50-75	-	ASTM D7028
	Heat distortion temperature (°C)	65	1.82 MPa	ASTM D648
		165	0.46 MPa	ASTM D648
15 wt% glass fiber reinforced PA6	Melting temperature (°C)	210-225	T_m, crystalline	-
	Glass transition temperature (°C)	50-75	-	ASTM D7028
	Heat distortion temperature (°C)	200	1.82 MPa	ASTM D648
		220	0.46 Mpa	ASTM D 648
30 wt% glass fiber reinforced PA6	Melting temperature (°C)	215-225	T_m, crystalline	-
	Glass transition temperature (°C)	50-75	-	ASTM D7028
	Heat distortion temperature (°C)	205	1.82 MPa	ASTM D648
		220	0.46 MPa	ASTM D648

c) Chemical resistance

Resistance is least to strong acids and phenols which are most effective at disrupting the hydrogen bonding and can sometimes dissolve the nylon. Highly polar materials, such as alcohols, are absorbed and sometimes dissolve the nylons containing lower concentrations of amide groups.

Ethylene glycol, which is used in engine coolants, is absorbed by nylon and dissolves PA6,6 (and PA6) above 160 °C. Certain metal salts can attack nylon causing stress cracking, e.g., zinc or calcium chloride, or even dissolve the material in alcoholic solution, e.g., lithium chloride [9].

Table 2.6 Chemical resistance of engineering thermoplastics [34]

Material	Ketone	Acid		Alkali	Alcohol	Hydrocarbons (aromatic)	Greases and oil
		Dilute	Conc.				
PET	-	G	P	G	F	G	G
PBT	-	G	F	G	G	G	G
PC	-	F/G	P	G	P	G	P
PMMA	G	F	G	F	P	P	P
ABS	-	G	F	-	P	-	P
PA6,6	P	P	G	G	G	G	G
PA6	P	P	G	G	G	G	G

<u>Note</u>: G = Good, F = Fair, P = Poor

2.2.3 Reinforcement for Nylon 6

Nylon 6 (PA6) is possibly reinforced with inorganic or organic materials. Basically, reinforcement of PA6 is done to provide the desired mechanical, physical and chemical properties [12]. Fillers used for reinforcement of nylon are usually in the form of fibers which normally include mineral fibers, glass fibers, carbon fibers, and para-aramid fibers (Kevlar). Carbon fibers give very high stiffness but are more expensive than glass fibers. While para-aramid fibers reinforcement with nylon can be used for applications requiring high abrasion resistance. Glass fibers are widely used to improve the physical and mechanical properties of many plastics. Moreover, glass fiber reinforcement also improves dimensional stability, stiffness, strength and heat resistance since the reinforcing materials are chemically bonded to PA6. These glass fibers are glued or bonded together by the plastic materials [29,35]. High aspect ratio of glass fiber is ideal for reinforcement. The nanolayers are not easily prepared due to their preferred face-to-face stacking in agglomerated attics and the fibers were damaged in the process. In nylon based thermoplastic, 70 wt% of glass fiber is a maximum loading of reinforcement due to limitation of standard compounding techniques. For automotive structural, 45-65 wt% glass fiber reinforced nylon are proper contents that give high modulus and strength [36,37].

Glass fibers offer several advantage over other materials when used as reinforcement [38]. These advantages can be summarized as follows:

- They are produced in a variety of form to suit particular end-used
- Good mechanical performance of the injection molded structural parts after several re-molding–re-grind cycles (property losses are minimal)
- Mould ability to close tolerances
- Reduced melt viscosity for faster processing
- High flow and toughness in thin sections, easy to fill complicated shapes of hollow parts
- Immune to microbiological attack
- Good resistance to most chemicals and weathering

- High dimensional stability
- High heat resistance

2.2.4 Application

Nylon is often formed into fiber and used for monofilament and yarn [22]. It can be made strong enough to stand up under the punishment tire cords must endure, fine enough for sheer, high fashion hosiery, and light enough for parachute cloth and backpacker's tents [23]. Nylon is considered as comfortable fiber in contact with the skin. From this property, nylon is made for clothing. Moreover, it is made into everyday product such as ropes, tents, toothbrush bristles, etc.

About 55% of nylon produced in the world is used in the transportation industries, and most of this use is concerned with automobile production. Automotive applications for nylons range from door handles, wheel covers to under-the-hood parts and electrical connectors. Nylon has been used to make the belts that reinforce tires. Most passenger car tires have steel belts, but tires for aircrafts, trucks and off-road vehicles are often made of nylon. It is also used for self-lubricating gears, bearings, air bag container, peddles and it has also been used to replace metal in seal system. Plasticized and glass reinforced nylons have replaced metal for fuel and vent lines and connectors. These grades of nylon offer much better corrosion resistance, better flexibility and higher impact resistance than the metal they replace [26].

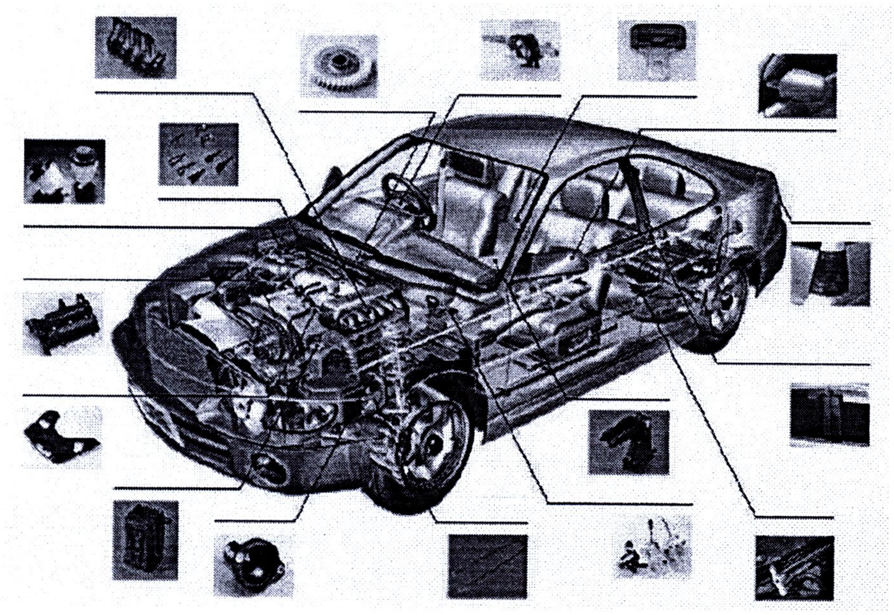


Figure 2.6 Nylon application for automobile [39]

The toughness, bending and tensile strength of nylon increase with increasing content of glass fiber while the shrinkage decreases. The 15 wt% glass fiber reinforced nylon is applied in automotive, electrical, engineering and consumer-good. High modulus/strength fiber-glass reinforced (with 45–65 wt% glass reinforced (GF)) nylon are emerging in automotive structural body panels, levers, internal and external mirror housings, seat frames, steering wheels, and various heavily stressed door handles [36]. One special application is the use of a nylon product as a fuel barrier material in polyethylene fuel tanks [9].

2.2.5 Processing

All nylons absorb moisture. The extent of moisture absorption depends on temperature, crystallinity, and humidity. Nylons need to be processed in dry condition to avoid molecular weight loss, bubble formation and significant polymer degradation during processing. Therefore, before processing of nylon resins, the polymer pellets must be dried to obtain moisture levels below 0.1-0.15 wt% for PA6,6 and PA6, 0.1 wt% for PA11 and PA12, and 0.05 wt% for nylon 4,6. The materials are normally supplied dry by the manufacture in moisture proof packaging such as foil-lined 25-kg bags or lined 1-

ton boxes. Material that has absorbed some moisture can be dried again using a vacuum oven at 80 °C or a dehumidifier hopper drier [9,23].

Material should not be processed at too high temperature, e.g., preferably not above 310 °C for nylon 6,6 and 290 °C for nylon 6, in order to avoid degradation. Residence times at the higher temperatures should be kept to minimum.

Table 2.7 Processing properties of nylon [30-32]

Material	**Processing properties**		**State**
PA6	Processing Temperature (˚C)	250-255	Injection
		227-274	Extrusion
	Molding Pressure (MPa)	30-60	Injection
	Cooling Time (sec)	10-15	Injection
15 wt% glass fiber reinforced PA6	Processing Temperature (˚C)	227-291	General
	Cooling Time (sec)	6-10	Injection
30 wt% glass fiber reinforced PA6	Processing Temperature (˚C)	238-288	Injection
	Cooling Time (sec)	2-5	Injection

2.2.6 Degradation

The -COOH and $-NH_2$ end-groups in nylons are sensitive to UV light, heat, oxygen, acids and alkali. When exposed to elevated temperatures, unmodified nylons undergo molecular weight degradation resulting in loss of mechanical properties. The degradation is highly time/temperature dependent. By adding heat stabilizer, nylon can be used at elevated temperature for long-term performance. Exposure to UV light results in degradation of nylon over an extended period of time; it appears that adding carbon black can reduce the radiation degradation [23].

2.3 Physical and Mechanical Properties Testing

2.3.1 Physical Properties

All nylons absorb moisture at different degree. The absorption process causes change in properties and dimensions [12]. Water will cause the polymer to swell and serves as a plasticizer, consequently lowering its performance, such as in electrical and mechanical behaviors. The standard tests ISO 62 and ASTM D570 are used to measure the water absorption of polymers. Factors affecting water absorption include: type of plastic, additives used, temperature and length of exposure. The data sheds light on the performance of the materials in water or humid environment. Mass change, diameter change, thickness change and volume change are determined under specified conditions.

Specimen size

Disk with 50.40 mm in diameter and 3.00 mm in thick is shown in Figure 2.7.

Data: Water absorption is expressed as increase in weight percent.

$$\text{Percent water absorption} = \left[\frac{\text{Wet weight - Dry weight}}{\text{Dry weight}}\right] \times 100$$

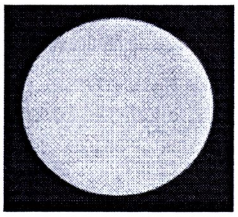


Figure 2.7 Specimen (disk) for Water Absorption, Mass Change, Diameter Change, Thickness change and Volume change [7,9]

2.3.2 Tensile Test

This test method covers the determination of the properties of plastics in standard dumbbell shaped test specimens. Tensile properties show the ability of a material to withstand a longitudinal stress[40].The tensile strength at yield of a material is the maximum amount of tensile stress that can be applied before the material permanently deforms. It is the first point on the stress-strain curve at which an increase in strain occurs without an increase in stress. This is a remarkable point for the engineering properties of the material since it may loose the loading capacity or it undergoes large deformations. The ultimate tensile strength (UTS) of a material is the limit stress where the material cracks grow [40].

Tensile test is the most common mechanical test performed on material science and mechanical engineering at a fixed temperature. From the data obtained, the tensile strength, yield point, elastic limit, modulus of elasticity, and other properties of the material can be collected [41]. Figure 2.8 illustrates the example of stress-strain curve.

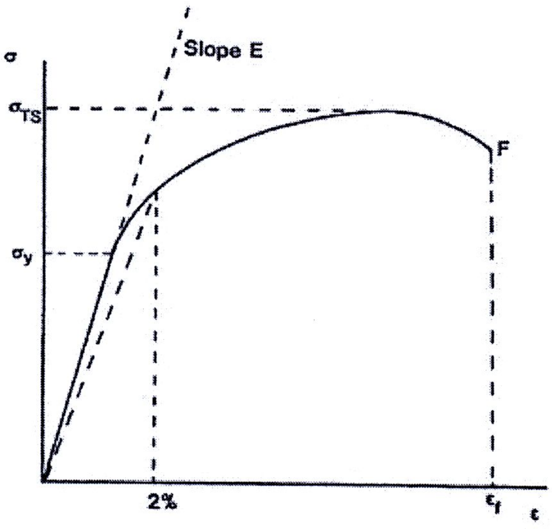


Figure 2.8 Schematic stress (σ) and strain (ε) curve [42].

Strain (ε), which can also be expressed in terms of engineering strain, is determined from the change in length of the sample compared with the original length shown as follows.

$$\varepsilon \text{ (engineering strain)} = \frac{\text{change in length}}{\text{original in length}} = \frac{\Delta L}{L}$$

Stress (σ) is the force at a given time divided by the original cross sectional area of the sample:

$$\sigma = \frac{F}{A}$$

where F is load applied [N]

A is cross sectional area [m^2]

The tensile strength of a sample is defined as the engineering stress at the onset of necking, or at break if no necking occurs. The Young's modulus is the slope of the initial line (linear portion) that gives the relationship of stress to strain and is a measure of the material's stiffness. In this linear region, the line obeys the relationship defined as "Hooke's Law" where the ratio of stress to strain is constant.

$$E = \frac{\sigma}{\varepsilon}$$

where E is Young's modulus

Frequently in polymers, there is no linear portion to the curve and tangent modulus (slope of a tangent to the stress-strain curve) or a secant modulus in which the slope of a line drawn from the origin to a specified (often 2%) strain value on the stress-strain curve is used to define a modulus. The yield stress is in principle the lowest stress which leads to permanent deformation after removal of the load. This is usually indicated by rapid change of slope in the curve but it can be difficult to determine. Hence, a stress at particular strain, often the stress at 2% offset strain, is then used to define a yield stress [42,43].

Test procedure

A minimum of five test specimens are prepared by machining operation or die cutting the materials in sheet, plate, slab or similar form. Specimens can also be prepared by injection or compression molding. The first step is placing of the specimen in the grips of the testing machine, taking care to align the long axis of the specimen and the grips with an imaginary line joining the points of attachment of the grips to the machine. Next is tightening the grips evenly and firmly to the degree necessary to prevent slippage of the specimen during the test [44]. The grips move apart at a constant rate. As the beam moves the force on the sample is recorded by the load cell and strain is measured using an extensometer. The practice of using the constant separation speed of the grips to determine sample strain is prone to errors since the testing machine itself will deflect under the applied load and slippage of the sample within the grips is not uncommon. Grips slippage can be abated or prevented by the use of roughened faces on the grips [9].

Specimen size

Recommended sample dimensions are set out in ISO 527-1 which is equivalent to ASTM D638. The ASTM recommended shape for a specimen test is illustrated in

Figure 2.9. The exact dimension depends on the thickness of the specimen and a few representative examples are shown in Table 2.8. At least five measurements are taken using universal testing machine. An average value and a standard deviation are statistically calculated.

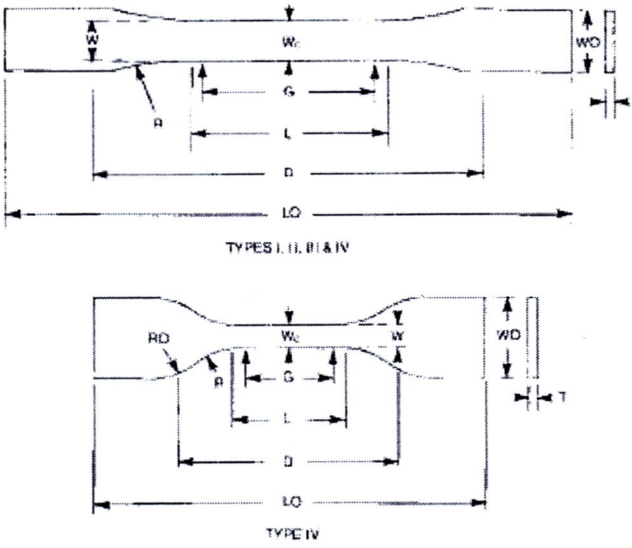


Figure 2.9 Standard tensile sample [44]

Table 2.8 Recommended tensile sample specimen dimensions for samples of the thicknesses indicated. All dimensions in mm [44]

	Thickness of sample					
Dimensions	7 or under		7 to 14	4 or under		Tolerances
	Type I	Type II	Type III	Type IV	Type V	
W	13	6	19	6	3.18	± 0.5
L	57	57	57	33	9.53	± 0.5
WO	19	19	29	19	9.53	± 6.4
LO	165	183	246	115	63.5	No max
G	50	50	50	-	7.62	± 0.25

Dimensions	7 or under		7 to 14	4 or under		Tolerances
	Type I	Type II	Type III	Type IV	Type V	
D	115	135	115	65	25.4	± 5
R	76	76	76	14	2.7	± 1
RO	-		-	25	-	± 1

2.3.3 Compression Test

The compression test is mainly used for determining the mechanical properties of unreinforced and reinforced rigid plastic. A compression test shows the behavior of materials under compressive loads. The specimen is compressed and deformation at various loads is measured [43]. Deformation for this test is the decrease in length produced in the gage length of the test specimen by a compressive load [45]. Compression test of ductile materials shows that the shape of stress-strain diagram depending considerably on the relative dimension of the specimen [29]. The compressive strength of the material is the maximum compressive stress exerted on the test specimens during a compression test. It may or may not be the compressive stress of the specimen at the moment of rupture [45].

Even in a compression test, there is a linear region where the material follows Hooke's Law. Hence for this region [46]

$$\sigma = \mathrm{E}\varepsilon$$

where E refers to the Young's Modulus for compression. By its basic definition the stress is given by:

$$\sigma = \frac{F}{A}$$

where F is load applied [N]

A is area [m^2]

Test procedure

The specimen is placed between compressive plates adjusted to parallel to the surface and constant rate of crosshead speed is controlled. In the testing of materials in compression it is assumed that the compressive force is uniformly distributed over the cross section. For stress the greatest care shall be taken in machining the ends, so that smooth flat parallel surfaces are obtained. This is due to the friction on the contact surfaces between the specimen and compression head of the testing machine that prevents the lateral expansion accompanying testing. The maximum load is recorded along with stress-strain data. An extensometer attached to the front of the fixture is used to determine strain and, hence, modulus [29,43].

Specimen size

The standard specimen size in compressive testing conforms to ASTM D 695. The specimen is in the form of a right cylinder or prism whose length is twice its width or diameter. Preferred specimen size is 12.7 x 25.4 x 12.7 mm^3 (W×L×D). Where elastic modulus and offset yield-stress data are desired, preferred specimen size is 12.7 x 50.8 x 12.7 mm^3 (W×L×D). For reinforced plastic, including high strength, the specimen size is 3.2 mm and over in thickness shall consist of a prism having cross section of 12.7 mm by the thickness and a length such that the slenderness ratio is in the range from 11:1 to 16:1 [45].

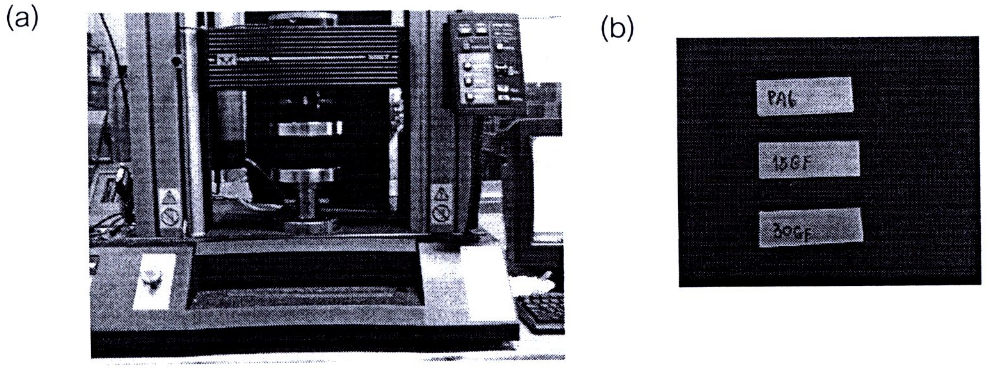


Figure 2.10 Universal testing machines for compression test (a); Specimen (rectangular) for compressive properties evaluation (b)

2.3.4 Flexural Test

The bending or flexural test, with various modifications, has been used as a standard test for various materials in specific applications. The mechanical properties that usually obtained from the flexural test are the flexural strength and flexural modulus. Flexural strength is the maximum flexural stress sustained by the test specimen during a bending test. Some materials, which are not broken at strains of up to 5%, should give a load deflection curve that shows a point at which the stress does not increase with an increase in strain. The above-mentioned point is called yield point. The flexural modulus is the slope of the initial line (linear portion) giving the relationship of stress to strain [29,47].

The classical cantilever, three point and four point bending tests, are particularly suitable for measurements of the modulus of brittle materials such as glassy polymer (see Figure 2.11). The modulus as a function of loading time by a force, F, is given by the following expression.

$$E(t) = FL^3/48aI$$

This equation refers to three point bending, with a the deflection, I the moment of inertia and L the distance as illustrated in Figure 2.11 b.

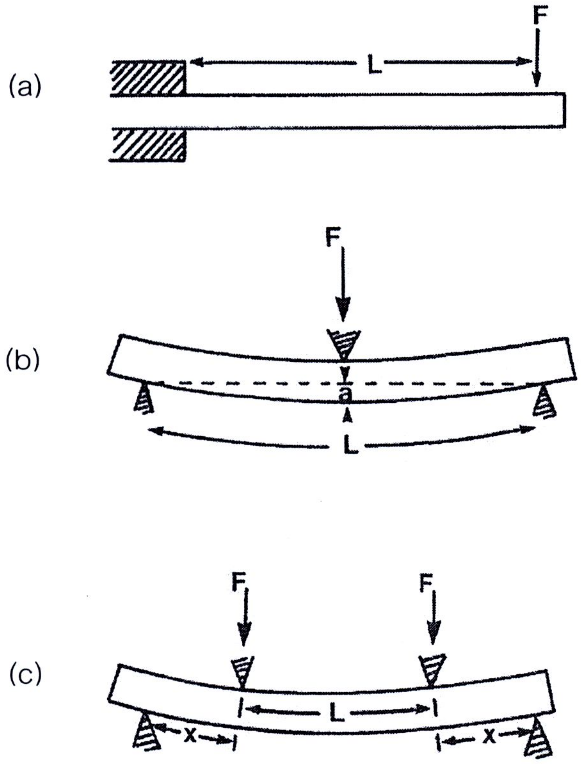


Figure 2.11 Flexural system, cantilever (a); three point bending (b); four point bending (c) [42]

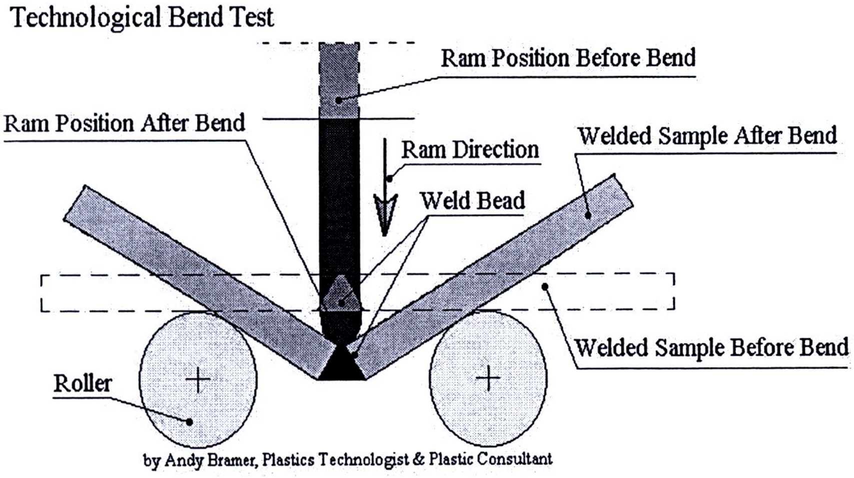


Figure 2.12 Technological three point bending test [48]

In general flexural measurement has an inherently lower accuracy than tensile test since the stress and strain vary across the thickness of the sample and cannot be unambiguously defined as in a tensile test. The simple flexural formula applies only to the case of small strain and this may be taken to mean a maximum strain in the beam of 5%. For a brittle material the fracture stress can be evaluated in a bending test by increasing the applied force in a three point bending test and noting the deflection at which fracture commences [42]. The maximum stress is given by

$$\sigma = \frac{3fL}{2wd^2}$$

where f is the ultimate center load

L is the span length

w is width of specimen

d is depth of specimen

Test procedure

Load is applied at a specified rate to the center of a rectangular cross section bar located on two supports. A support span-to-dept ratio is 16:1. The specimen is deflected until rupture occurs in the outer surface of the test specimen or until a maximum strain of 5.0% is reached, whichever occurs first. For high strength reinforced composite, the span-to-dept ration is chosen when the failure occurs in the outer fibers of the specimens with span-to-dept ratio larger than 16:1 (32:1 or 40:1 are recommended) [43,47].

Specimen size

The specimen size for flexural testing conforms to ASTM D 790 (Flexural Properties of Unreinforced and Reinforced Plastic). The specimen may be cut from sheet, plate, or molded shape, to the desired finished dimensions. A variety of specimen shapes can be used for this test, but the most commonly used specimen size is 12.7 x 64 x 3.2 mm^3 (W×L×D) complying with ASTM D790.

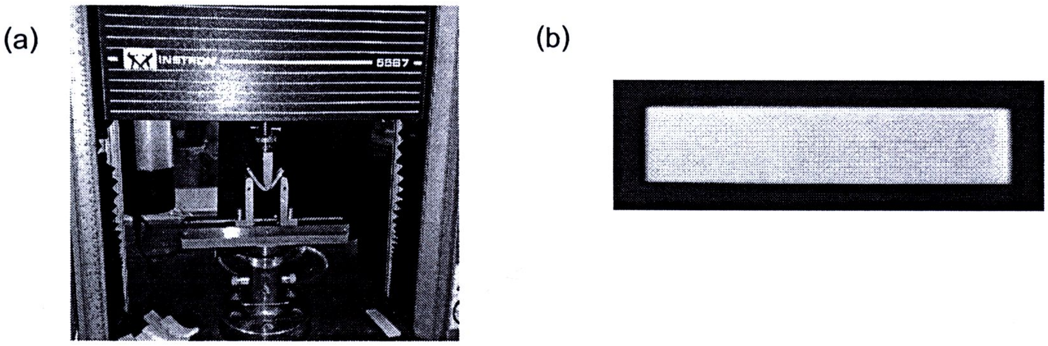


Figure 2.13 Universal testing machines for flexural test (a);Specimen bar for flexural test (b) [49]

2.3.5 Impact Test

The notched impact test is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. In the notched impact test, a notch is cut into the specified specimen dimension. By notching, a stress concentration as well as an increase in crack propagation rate is achieved at the front of the crack tip. In this way, a break can be achieved even on tough plastics that do not break when unnotched specimens are used [41,50].

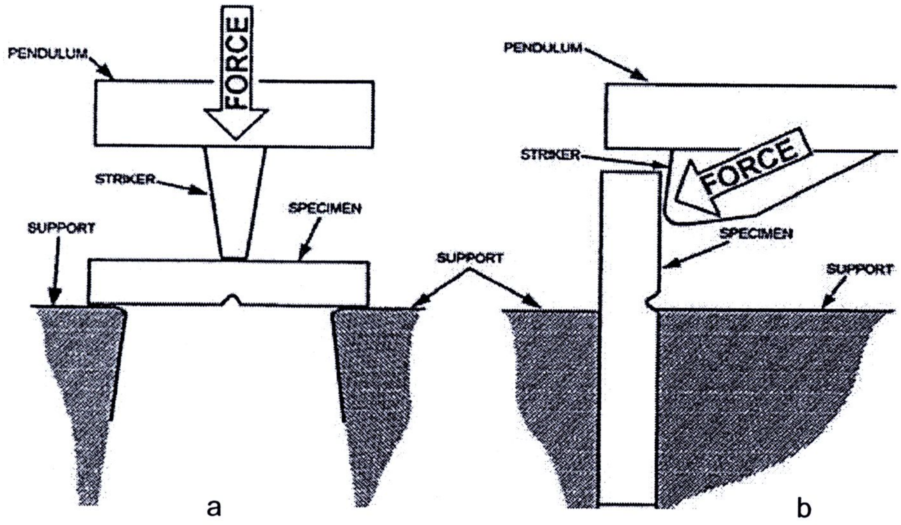


Figure 2.14 The kinds of specimens for impact testing Charpy (a); Izod (b) [41]

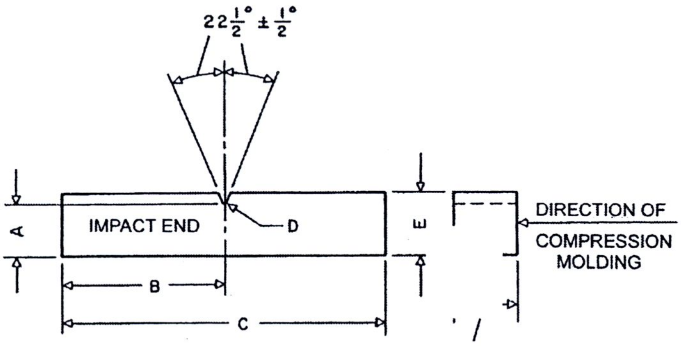
The two kinds of specimens used for impact testing are known as Charpy and Izod. Both test pieces are broken in an impact testing machine. The only difference is in the manner that they are anchored. The Charpy piece is supported horizontally between two anvils and the pendulum strikes opposite the notch, as shown in Figure 2.14(a). The Izod piece is supported as a vertical cantilever beam and is struck on the free end projecting over the holding vise Figure 2.14(b). Izod specimen is notched to prevent deformation of the specimen upon impact. For the test, pendulum hammers are used with nominal impact energies of 0.5 J to 50 J with an impact velocity of 3.5 m/s in Izod configuration [41,50,51].

Izod test procedure

The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen, shown in Figure 2.16(a), and this force can be seen on an impact-measuring gauge. If breakage does not occur, a heavier hammer is used until failure occurs. From ASTM impact energy is expressed in J/m or ft-lb/in. Impact strength is calculated by dividing impact energy by the thickness of the specimen. At least five, preferably 10 specimens, are prepared from sheets, composites, or molded specimens [43].

Specimen size

The bar shaped specimens are prepared for Izod impact strength testing following ASTM D256 (or ISO 180) as shown in Figure 2.16 (b). The specimens may be cut from sheets, plates, or molded shapes, and then molded to the desired finished dimensions. For sheet materials, the specimens are cut from the sheet in both the lengthwise and crosswise direction unless otherwise specified. The standard specimen for ASTM is 12.7±0.20 x 63.5±2.0 x 3.2 mm^3 (W×L×D). The angle of the notch is 45±1° with a radius of curvature at the apex of 0.25±0.05 mm. The dept of the plastic material remaining in the specimen under the notch is 10.16±0.05 mm. Impact tester is shown in Figure 2.16 (a).



A	10.16 ± 0.05 mm
B	31.8 ± 1.0 mm
C	63.5 ± 2.0 mm
D	0.25R ± 0.05
E	12.70 ± 0.20 mm

Figure 2.15 Dimension of impact test specimen ASTM D256 [52]

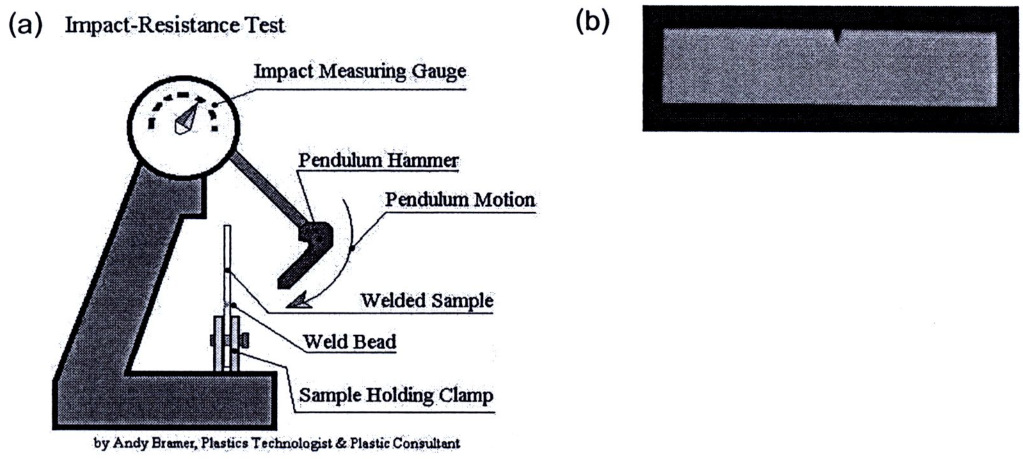


Figure 2.16 Izod impact testing (a); Bar shape specimen for Izod Impact Test (b) [9]

2.4 Thermal Properties Testing

2.4.1 Dynamic Mechanical Analysis (DMA)

DMA is a technique that does not require a lot of specialized training to use for material characterization. It supplies information about major transitions as well as secondary and tertiary transitions not readily identifiable by other methods. The DMA determines changes in sample properties resulting from changes in five experimental variables: temperature, time, frequency, force, and strain. The deformation can be applied sinusoidally under a fixed rate. It also allows characterization of bulk properties directly affecting material performance.

In DMA, a complex modulus (E*), an elastic modulus (E'), and an imaginary (loss) modulus (E") are recorded from the material response to the sine wave. These different moduli allow better characterization of the material, i.e., the ability of the material to return or store energy (*E*'), its ability to lose energy (*E*"), and the ratio of these effects (tan delta), which is called damping factor (tan δ). The storage modulus, E' (elastic response) and loss modulus, E" (viscous response) of polymers are measured as a function of temperature or time as the polymer is deformed under an oscillatory load (stress) at a controlled temperature in a specified atmosphere. The storage modulus is related to stiffness, and the loss modulus is related to damping and energy dissipation. Some details of polymer structure can be inferred from the result.

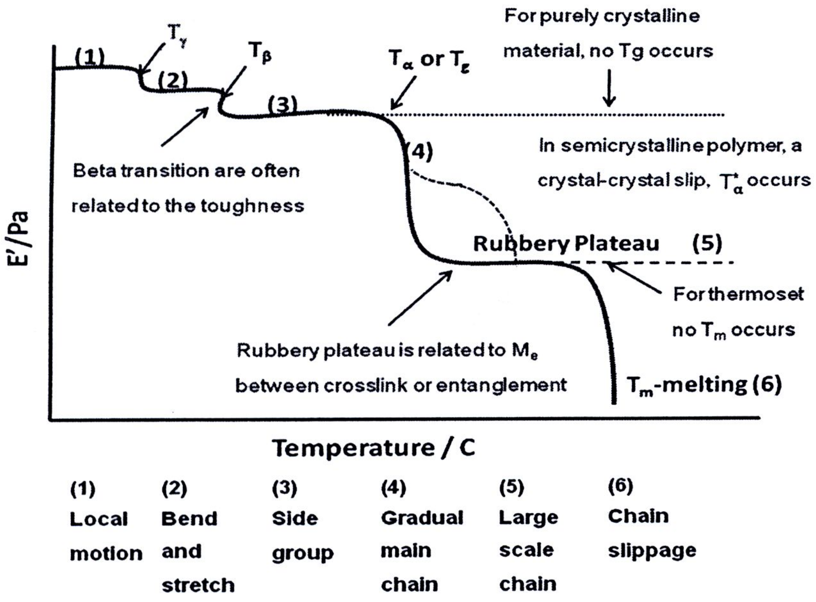


Figure 2.17 An idealized DMA scan showing the type of transitions [53]

The drop in E' and peak in tan δ is the glass transition temperature (T_g). These transitions are labeled by counting back from melting temperature, so the T_g here is also the alpha transition (T_α). As the T_g or T_α can be assigned to gradual chain movement, so the beta transition (T_β) can be assigned to branch chain or pendant group movements and can often be related to the toughness of a polymer. The difference in the area of the T_β peak in the tan δ and the size relative to the T_g of T_β reveal to impact via localized chain movements of materials. In the range between T_g and T_β the material possesses the stiffness to resist deformation and the flexibility to not shatter under strain. The T_g represents a major transition for many polymers, as physical properties change drastically as the material goes from a hard glassy to rubbery state. It defines one end of the temperature range over which the polymer can be used, often called the operating range of the polymer.

Additionally, the T_g is often measured by Differential Scanning Calorimetry (DSC), but the DMA technique is more sensitive and yields more easily interpreted data.

DMA can also be used to investigate the frequency (and therefore time) dependent nature of the transition. This is usual as the degree of dependence is specific to the transition type. The T_g has a strong dependence on frequency but melting temperature is frequency independent. DMA can also resolve sub-T_g transitions, like beta (β) and gamma (γ) transitions, in many materials while the DSC technique is not sensitive enough to pick up.

Test procedure

A flat rectangular specimen is placed in the DMA equipment and oscillated at a nominal frequency of 1 Hz. The two kinds of method used for glass transition temperature testing are known as three point bending mode and tension mode. The specimen is heated at rate of 5±1 °C/min. The temperature at which a significant drop in storage modulus (E') begins is assigned as the glass transition temperature (DMA T_g). The peak temperature of the tangent delta curve is identified along with DMA T_g for comparison purposes [54].

Specimen size

The flat rectangular specimens are prepared for glass transition temperature testing following ASTM D 7028 as shown in Figure 2.18(b). The specimens may be cut from sheets, plates, or molded shapes, and then molded to the desired finished dimensions. The standard specimen size for ASTM D 7028 is not fixed by this method; various dynamic mechanical analyzers require different sizes. Depending on the analyzer, typical specimen size can range from $56\pm4\times12\pm1\times2.0\pm0.5$ mm^3 (L×W×T) to $22\pm1\times3\pm1\times1.0\pm0.5$ mm^3 [54].

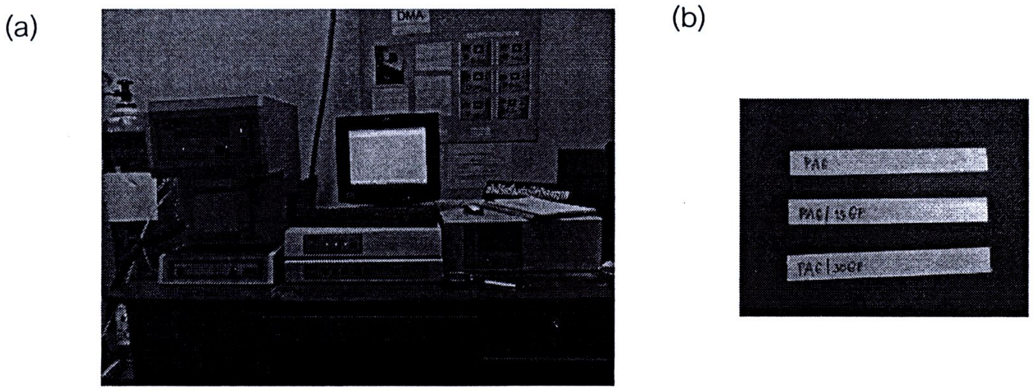


Figure 2.18 Dynamic mechanical analysis (a); Rectangular shape specimen for DMA test (b)

2.4.2 Heat Distortion Temperature (HDT)

Heat distortion temperature is defined as the temperature at which a standard test bar deflects a specified distance under load. It is used to determine short term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperature and those that lose their rigidity over a narrow temperature range.

Test procedure

A bar with rectangular cross section is tested in the edgewise position as a simple beam with the load applied at its center to give maximum fiber stresses of 0.455 MPa (66 psi) or 1.82 MPa (264 psi). The support span is either 100 mm or 101.6 mm. Load is applied to the center of specimen and then immersed into a silicone oil bath provided with a means of raising the temperature at 2 ± 0.2°C/min. The temperature of the medium is measured when the test bar has deflected of 0.25 mm (0.010 in.). This temperature is recorded as the heat distortion temperature under flexural load of the test specimen.

Specimen size

The specimens for heat distortion temperature testing conform to ASTM D 648. This test method applies to molded and sheet materials available in thickness of 3 mm or greater. The specimens may be cut from sheets, plates, or molded shapes. At least two test specimens are used to test each sample. The specimen is 127 mm in length, 13 mm in depth by any width from 3 mm to 13 mm. Tolerances on dimensions should be in the order of ± 0.13 mm over the length of the specimen [55].

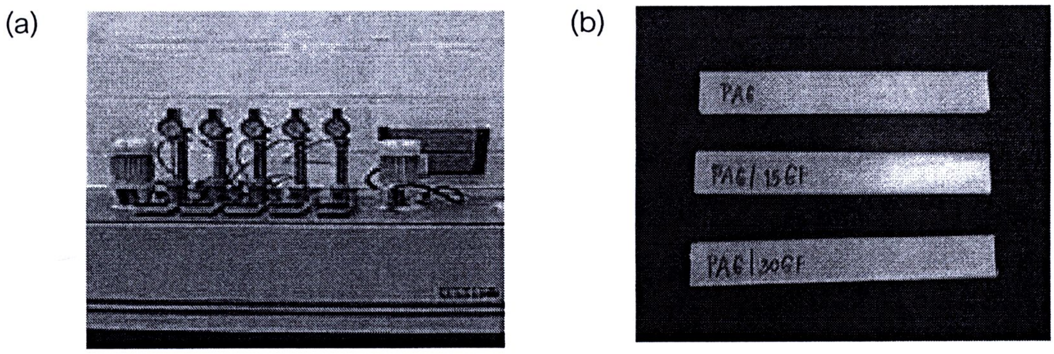


Figure 2.19 HDT/vicat (a); Rectangular shape specimen for HDT test (b)